

CHROMIAN ANDRADITE AND OLIVINE-CHROMITE RELATIONS IN A CHROMITITE LAYER FROM THE JIJAL COMPLEX, NORTHWESTERN PAKISTAN

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ABSTRACT

Green chromian andradite occurs associated with chrysotile in a chromitite layer within the dunite of the Jijal alpine ultramafic complex (northern Pakistan). The garnet contains, on average, 10.1 wt. % Cr_2O_3 (range 9.2–11.6%) and has a formula $\text{Ca}_{3.04}(\text{Cr}_{0.67}\text{Fe}^{3+}_{1.29}\text{Al}_{0.02})\text{Si}_{2.98}\text{O}_{12}$. The garnet formed during retrograde greenschist-facies metamorphism of the Jijal complex.

Keywords: chromian andradite, dunite, Jijal complex, Pakistan, retrograde metamorphism.

SOMMAIRE

On décrit une andradite verte chromifère associée au chrysotile dans un niveau de chromitite situé dans la dunite du complexe ultramafique alpin de Jijal (Nord-Ouest du Pakistan). Le grenat contient de 9.2 à 11.6% (en poids) de Cr_2O_3 (10.1% en moyenne), et sa composition globale est $\text{Ca}_{3.04}(\text{Cr}_{0.67}\text{Fe}^{3+}_{1.29}\text{Al}_{0.02})\text{Si}_{2.98}\text{O}_{12}$. Le grenat se serait formé lors du métamorphisme rétrograde du complexe dans le faciès schiste vert.

(Traduit par la Rédaction)

Mots-clés: andradite chromifère, dunite, complexe de Jijal, Pakistan, métamorphisme rétrograde.

INTRODUCTION

Chromian andradite occurs in a chromitite layer in dunite of the Jijal complex, which constitutes a part of the approximately 24000 km² Kohistan tectonic zone of the northwestern Himalaya of northern Pakistan; the zone comprises a variety of plutonic and volcanic rocks (mainly calcalkaline) and minor (meta) sediments. Tahirkheli *et al.* (1979) proposed that the zone represents an island arc turned on end during the Himalayan orogeny. Our more recent work (Coward *et al.* 1982) suggests that the Cretaceous Kohistan island arc became an Andean-type margin during the Eocene. The Jijal complex is a fault-bounded wedge about 200 km² in area situated on the Main Mantle Thrust, which is an extension of the Indus-Zangbo suture that marks the locus of subduction of the Indian plate under the Tibetan mass. The complex was described in detail by Jan (1979) and Jan & Howie (1981). It is composed principally of garnet granulite and a slab of

alpine ultramafic rocks up to 4 km thick. The granulites are ultrabasic to intermediate, with garnet + clinopyroxene + plagioclase + quartz + rutile ± hornblende ± epidote as the most common assemblage. Jan & Howie suggested that the granulites were metamorphosed at 690–770°C and 12–14 kbar. Retrograde paragonite (with 100 Na/(Na + K) up to 98.7) formed during the uplift of the granulites at 510–550°C, 8–9.5 kbar (Jan *et al.* 1982).

The alpine ultramafic rocks consist of diopsidite, peridotite, dunite and websterite, all devoid of plagioclase and garnet. Estimates of temperature (800–850°C) and pressure (8–12 kbar) suggest metamorphism under granulite-facies conditions. Field and geochemical data indicate that the ultramafic rocks are not comagmatic with the garnet granulites. Jan & Howie (1981) proposed that the ultramafic rocks were emplaced as plastic material in the granulites before the entire mass was obducted against the Indian plate along the Main Mantle Thrust.

The ultramafic rocks contain disseminated chromite as well as chromitite stringers, layers and lenses. Geologists of the Sarhad Development Authority (pers. comm.) report that pyroxenites, dunites and peridotites host the chromitites. Based on a study of over 60 concentrations, they estimate about 0.37 million metric tonnes of reserves. The chromite bodies are randomly distributed; however, clustering of bodies does occur locally, such as to the north of Jijal, near Mandirara. Many of the chromite-rich zones show folds, faults, shear zones and boudinage, caused either by ductile emplacement or later deformation. The largest chromite-rich zone is over 100 m long and consists of many lenses of various sizes. The largest lens is 40 × 5 m. This paper describes the unusual association of chromian andradite and serpentine, which occurs in a 10-cm-thick layer of chromitite in dunite to the north of Jijal (35° 05'N, 72° 55'E) and south of the main occurrence of chromitites.

PETROGRAPHY

The chromitite layer containing the chromian an-

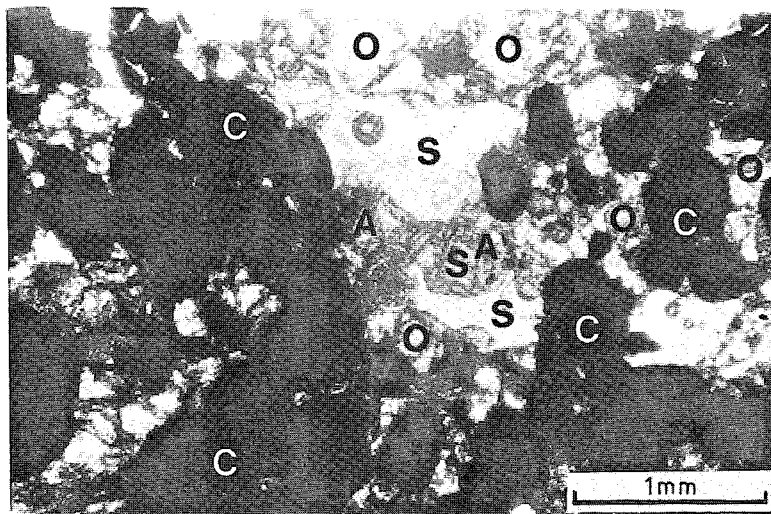


FIG. 1. Microphotograph of the main occurrence of chromian andradite in chromitite. A andradite, O olivine, C chromite, S serpentine.

dradite has sharp contacts with its dunitic host-rock. The chromitite consists of chromite (up to 80–90% modal) and 10–20% olivine. The densely packed grains of chromite have euhedral to subhedral shapes typical of cumulate; olivine forms postcumulus anhedral grains between them.

In Figure 1, there are six groups of bright green andradite grains within an area of 0.5×0.5 cm. The andradite forms subhedral to anhedral grains up to 0.1 – 0.2 mm in diameter between the chromite and olivine grains. The largest grains are subhedral and occur in two veinlets up to 0.2 mm wide and 1 mm long, associated with grey cross-fibre chrysotile. The largest grain of andradite has an inclusion of olivine. Garnet and chrysotile are the only secondary minerals. Rare chrysotile grains occur elsewhere in the chromitite.

MINERAL CHEMISTRY

The analyses were performed at the University of Leicester with a Cambridge Microscan 5 microprobe. Results of wavelength-dispersion analyses of the garnet are presented in Table 1. Results of energy-dispersion analyses of chromite and olivine from the chromitite and dunite and of serpentine are given in Table 2. In the case of chromite and olivine, the core and margin of two grains of each mineral were analyzed to check for compositional variations within and among grains.

Garnet

The composition is variable with respect to Cr and Fe in the ten point-analyses. Charge-balance con-

siderations suggest that all the iron is present in trivalent form. The quantities of Mg, Ti, and Al are very low, and Mn is below the detection limit in all but two cases. A simplified formula for the mineral is $\text{Ca}_{3.02-3.05}(\text{Cr}_{0.61-0.77}\text{Fe}^{3+}_{1.21-1.36}\text{Al}_{0.01-0.03}\text{Si}_{2.97-3.00}\text{O}_{12})$, with a mean for ten point-analyses of $\text{Ca}_{3.04}(\text{Cr}_{0.67}\text{Fe}^{3+}_{1.29}\text{Al}_{0.02}\text{Si}_{2.98}\text{O}_{12})$. Because it appears that Ca is slightly overestimated relative to the trivalent cations, the analyses were checked by energy dispersion using the microprobe facility in the Department of Mineralogy and Petrology at the University of Kiel, West Germany; these analyses give an identical result within experimental error. Us-

TABLE 1. REPRESENTATIVE COMPOSITIONS OF GARNET, JIJAL COMPLEX

	1	2	3	4	Mean	2 σ
SiO ₂ wt.%	35.60	35.64	35.63	35.70	35.62	0.13
TiO ₂	0.07	0.09	0.14	0.12	0.12	0.07
Al ₂ O ₃	0.29	0.30	0.10	0.21	0.21	0.17
Cr ₂ O ₃	9.43	9.23	9.53	11.60	10.11	1.47
Fe ₂ O ₃	20.91	20.67	21.57	19.24	20.48	1.44
MnO	-	-	-	0.03	-	-
MgO	0.14	0.15	0.10	0.14	0.13	0.04
CaO	33.87	33.90	33.78	33.87	33.86	0.09
Total	100.31	99.98	100.85	100.91	100.53	
Oxygen	12	12	12	12	12	
Si	2.985	2.996	2.977	2.976	2.981	
Ti	0.004	0.006	0.009	0.008	0.008	
Al	0.029	0.030	0.010	0.021	0.021	
Cr	0.625	0.613	0.629	0.765	0.669	
Fe ³⁺	1.320	1.307	1.356	1.207	1.290	
Mn	-	-	-	0.002	-	
Mg	0.017	0.019	0.012	0.017	0.016	
Ca	3.043	3.053	3.024	3.025	3.037	

End members [mean, recalculated by method of Rickwood (1968)] Andradite 65.2, uvarovite 33.8, pyrope 0.5, grossular 0.5. All mean values, standard deviation and ranges based on 10 point-analyses, obtained by electron microprobe; R.N. Wilson analyst.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF CHROMITE, OLIVINE AND SERPENTINE, JIJAL COMPLEX

	Chr(D ₄)	Chr(C ₄)	Ol(D ₄)	Ol(C ₁)	Srp(2)
SiO ₂ wt. %	0.33	0.36	41.46	42.29	41.88
TiO ₂	0.12	0.18	0.05	0.04	0.00
Al ₂ O ₃	7.57	7.80	0.08	0.28	0.16
Cr ₂ O ₃	59.09	60.77	0.11	0.21	0.35
Fe ₂ O ₃	3.86	3.63	-	-	-
FeO	16.90	15.17	4.31	3.78	1.74
MnO	0.49	0.40	0.07	0.13	0.00
MgO	10.44	12.04	52.09	53.92	39.31
NiO	-	-	0.46	0.49	-
Total	98.80	100.35	98.63	101.14	83.44
Oxygen	4	4	4	4	7
Si	0.011	0.012	1.005	0.998	2.027
Ti	0.003	0.004	0.001	0.001	0.000
Al	0.301	0.302	0.002	0.008	0.009
Cr	1.573	1.576	0.002	0.004	0.013
Fe ³⁺	0.098	0.090	-	-	-
Fe ²⁺	0.476	0.416	0.087	0.075	0.070
Mn	0.014	0.011	0.001	0.003	0.000
Mg	0.524	0.589	1.883	1.898	2.836
Ni	-	-	0.009	0.009	-

Total iron was determined as FeO. In chromite, the ratio of Fe³⁺ to Fe²⁺ is adjusted such that $3^{3+} + 2^{2+} = 2:1$. In olivine and serpentine, all iron was taken to be Fe²⁺. Number in parentheses indicates number of point analyses; M. Q. Jan analyst. Serpentine total includes 0.11% Na₂O, giving 0.010 Na in the formula. D dunite, C chromitite. Chr chromite, Ol olivine, Srp serpentine.

ing the recalculation scheme of Rickwood (1968), 98.7% of the cations can be assigned to the end-members andradite (65.2) and uvarovite (33.8), with a small amount of pyrope (0.5) and grossular (0.5).

The composition of the garnet is unusual. Most specimens of chromian garnet are a solid solution of uvarovite and grossular end-members; only in very few instances has chromian andradite been reported. Our survey of *Mineralogical Abstracts* for the past fifteen years reveals only two occurrences of chromian andradite: Val Malenco, Italy (Amthauer *et al.* 1974) and Nizhny Tagilsk in the Urals (Rost *et al.* 1979). The Cr₂O₃ content of the Malenco garnet is $\leq 1.3\%$, and the estimated conditions of formation are 370°C and 0.5 to 1.5 kbar. The Urals garnet has comparatively higher Cr₂O₃ (up to 3.9%). More recently, Duke & Bonardi (1982) described a very similar garnet to that of Jijal, from Réaume Township, in Ontario; it coexists with 5% (modal) chromite and formed at greenschist-facies temperatures. The Cr₂O₃ content of this garnet ranges widely (0.53 - 10.54%); some values are slightly higher than in the Jijal garnet, but the average Cr₂O₃ of 29 determinations is about 3% lower than in Jijal. A significant difference with the Jijal garnet is that the Réaume garnet is much richer in Al (2.05 versus 0.18 Al₂O₃).

On thermodynamic reasoning, Ganguly (1976) predicted the presence of a solvus between uvarovite and andradite end-members of the ugrandite series, and suggested that compositions of naturally occurring garnet are in agreement with this. However, the more recent chemical data of Duke & Bonardi (1982) "suggest rather extensive solid solution at low temperature (up to at least 40% uvarovite)"; our four compositions agree with this view.

Chromite

The compositions of chromite from the dunite and chromitite are similar. Both are very rich in Cr, and there appears to be no notable chemical variations from grain to grain. However, the chromite from the dunite has a slightly lower Al/ ΣR^{3+} , and higher Fe²⁺/Mg in the margin than in the core (180 μ m distance). A similar pattern is seen in the chromite from the chromitite, but in one grain Al does not vary from core to margin. The variation, however, is within the limits of analytical error. Both compositions are typical of alpine chromite, except that such chromite is somewhat more Fe-rich (Irvine 1967, Thayer 1970).

Olivine, and its Mg-Fe distribution with chromite

The composition of olivine in dunite is very similar to that in chromitite. However, in the chromitite, the olivine has higher Al, Cr and Mn. Chromium is considered as divalent, following recent investigations (for details, see Brown 1980). The ratio 100 Mg/(Mg + Fe²⁺) of the olivine in dunite is 95.6, only slightly lower than that in the chromitite (96.2). Both values are markedly higher than those reported elsewhere in Jijal (Jan & Howie 1981) and in other alpine peridotite complexes (the values range between 89 and 93). However, similar values have been reported from occurrences of some alpine chromitite, for example, the Tari-Misaka complex in western Japan (Arai 1979) and the Vulcan Peak peridotite, Oregon (Himmelberg & Loney 1973).

An increase in the forsterite content of olivine with increasing modal proportion of chromite has been recorded in some complexes, such as Vulcan Peak (Himmelberg & Loney 1973) and the eastern Bushveld Complex (Cameron 1975). Irvine (1967) suggested that where olivine and chromite crystallize from a magma, a small-scale exchange of Mg and Fe²⁺ may take place between them. Where chromite is a minor constituent, it becomes appreciably richer in Fe²⁺ as the rock cools, whereas the silicate mineral remains relatively constant in composition. Where the silicate is subordinate, it becomes more magnesian, whereas the chromite changes only slightly. The higher Fe content of the chromite in the Jijal dunite layer and the higher Mg content of the olivine in the chromitite are in agreement with this suggestion. However, the amounts of chromite in the dunite are not sufficient to explain the variation from Fo₉₀ in dunite distant from chromitite to Fo₉₆ in dunite associated with chromitite. We suggest that this variation reflects loss of Fe to chromite as a result of ionic diffusion across the layers. The closeness in the compositions of accessory and dominant chromite and olivine supports this.

Temperature estimates based on the Mg-Fe²⁺

distribution between the olivine and chromite, and the Cr content of the chromite in the Y site (also taking into consideration the Fe^{3+} content in this site) are approximately 950, 800, 750 and 650°C by the methods of Medaris (1975), Evans & Frost (1975), Fabriès (1979) and Fujii (1977), respectively. The last method gives an erroneous estimate of temperature and requires revision, as suggested by Fabriès. From various silicate geothermometers, Jan & Howie (1981) calculated that the Jijal ultramafic rocks had undergone granulite-facies metamorphism between 800 and 850°C.

Serpentine

The serpentine composition is the average of two very similar sets of analytical data. Considering the fact that serpentine contains about 13% H_2O , it appears that the total is low by 2 to 3%. The composition of the Jijal mineral is closer to the average chrysotile than to lizardite or antigorite (*cf.* Page 1968, Whittaker & Wicks 1970). Chrysotile typically is fibrous, and the Jijal serpentine consists of slightly curved fibres. The Jijal grains are optically length-slow; this confirms the determination as chrysotile.

The stability limits of chrysotile are not clearly known. Coleman (1971) and Caruso & Chernosky (1979) suggested that it forms at lower temperatures than the other two serpentine minerals. Recent experimental data, summarized by Moody (1976), indicate that chrysotile crystallizes on the low-temperature side of reactions in the range from 525°C at 7 kbar $P(H_2O)$ to 380°C at 0.2 kbar $P(H_2O)$ (Chernosky 1973).

SUMMARY AND DISCUSSION

Chromian andradite and associated chrysotile occur in a chromitite seam in dunite of the Jijal complex. The compositions of chromite from both the dunite and chromitite layers resemble those from other alpine complexes, except that they are somewhat more Fe-rich. Moreover, the olivine compositions are highly magnesian (Fe_{96}). The distribution of Fe and Mg between the two phases is consistent with equilibration temperatures of about 800°C.

During obduction along the Main Mantle Thrust (Indus Suture), the complex locally underwent lower-P-T re-equilibration, giving rise to paragonite-bearing assemblages calculated to have formed at 510–550°C and 8–9.5 kbar in the garnet granulites (Jan *et al.* 1982). Further obduction caused even lower-P-T assemblages, and led to local serpentinization of the ultramafic rocks. The chromian andradite – chrysotile assemblage developed under greenschist-

facies conditions at temperatures of less than 380–525°C (depending on the pressure). We have no means of deducing a pressure. Amthauer *et al.* (1974) suggested 370°C and 0.5–1.5 kbar for an Italian chromian-andradite-bearing serpentinite. Because the Jijal rock does not contain any Ca-bearing phase, some Ca (and, possibly, Si) must have been added from an external source during the formation of garnet in the serpentinite.

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REFERENCES

- AMTHAUER, G., KURTZ, W., ROST, F. & SCHLOEMER, H. (1974): Chemismus und Genese des Andradits aus dem Serpentin des Val Malenco (Bernina-Gebiet/Oberitalien). *Schweiz. Mineral. Petrol. Mitt.* **54**, 691-706.
- ARAI, S. (1979): Polygenetic olivines in chromitite from the Tari-Misaka ultramafic complex, western Japan. *Rep. Fac. Sci. Shizuoka Univ.* **13**, 105-114.
- BROWN, G.E., JR. (1980): Olivines and silicate spinels. In *Orthosilicates* (P.H. Ribbe, ed.). *Mineral. Soc. Amer., Rev. Mineral.* **5**, 275-381.
- CAMERON, E.N. (1975): Postcumulus and subsolidus equilibration of chromite and silicates in the eastern Bushveld Complex. *Geochim. Cosmochim. Acta* **39**, 1021-1033.
- CARUSO, L.J. & CHERNOSKY, J.V., JR. (1979): The stability of lizardite. *Can. Mineral.* **17**, 757-769.
- CHERNOSKY, J.V., JR. (1973): The stability of chrysotile, $Mg_3Si_2O_5(OH)_4$, and the free energy of formation of talc, $Mg_3Si_4O_{10}(OH)_2$. *Geol. Soc. Amer. Abstr. Programs* **5**, 575.
- COLEMAN, R.G. (1971): Petrologic and geophysical nature of serpentinites. *Geol. Soc. Amer. Bull.* **82**, 897-918.
- COWARD, M.P., JAN, M.Q., REX, D., TARNEY, J., THIRLWALL, M. & WINDLEY, B.F. (1982): Geotectonic framework of the Himalaya of N Pakistan. *J. Geol. Soc. London* **139**, 299-308.
- DUKE, J.M. & BONARDI, M. (1982): Chromian andradite from Réaume Township, Ontario. *Can. Mineral.* **20**, 49-53.

- EVANS, B.W. & FROST, B.R. (1975): Chrome-spinel in progressive metamorphism - a preliminary analysis. *Geochim. Cosmochim. Acta* **39**, 959-972.
- FABRIÈS, J. (1979): Spinel-olivine geothermometry in peridotites from ultramafic complexes. *Contr. Mineral. Petrology* **69**, 329-336.
- FUJII, T. (1977): Fe-Mg partitioning between olivine and spinel. *Carnegie Inst. Wash. Yearb.* **76**, 563-569.
- GANGULY, J. (1976): The energetics of natural garnet solid solution. II. Mixing of the calcium silicate end-members. *Contr. Mineral. Petrology* **55**, 81-90.
- HIMMELBERG, G.R. & LONEY, R.A. (1973): Petrology of the Vulcan Peak alpine-type peridotite, southwestern Oregon. *Geol. Soc. Amer. Bull.* **84**, 1585-1600.
- IRVINE, T.N. (1967): Chromian spinel as a petrogenetic indicator 2. Petrologic applications. *Can. J. Earth Sci.* **4**, 71-103.
- JAN, M.Q. (1979): Petrography of the Jijal complex, Kohistan. *Geol. Bull. Univ. Peshawar (Spec. Issue)* **11**, 31-50.
- _____ & HOWIE, R.A. (1981): The mineralogy and geochemistry of the metamorphosed basic and ultrabasic rocks of the Jijal complex, Kohistan, NW Pakistan. *J. Petrology* **22**, 85-126.
- _____, WILSON, R.N. & WINDLEY, B.F. (1982): Paragonite paragenesis from the garnet granulites of the Jijal complex, Kohistan, N. Pakistan. *Mineral. Mag.* **45**, 73-77.
- MEDARIS, L.G., JR. (1975): Coexisting spinel and silicates in alpine peridotites of the granulite facies. *Geochim. Cosmochim. Acta* **39**, 947-958.
- MOODY, J.B. (1976): Serpentinization: a review. *Lithos* **9**, 125-138.
- PAGE, N.J. (1968): Chemical differences among the serpentine "polymorphs". *Amer. Mineral.* **53**, 201-215.
- RICKWOOD, P.C. (1968): On recasting analyses of garnet into end-member molecules. *Contr. Mineral. Petrology* **18**, 175-198.
- ROST, F., FUCHS, B. & SADDREDINI, H. (1979): Über Demantoid aus dem Ural und seine Farbe. *Aufschluss* **30**, 51-66.
- TAHIRKHELI, R.A.K., MATTAUER, M., PROUST, F. & TAPPONNIER, P. (1979): The India-Eurasia suture zone in northern Pakistan: synthesis and interpretation of recent data at plate scale. In *Geodynamics of Pakistan* (A. Farah & K.A. DeJong, eds.). Geol. Surv. Pakistan, Quetta, Pakistan.
- THAYER, T.P. (1970): Chromite segregations as petrogenetic indicators. *Geol. Soc. S. Afr. Spec. Publ.* **1**, 380-390.
- WHITTAKER, E.J.W. & WICKS, F.J. (1970): Chemical differences among the serpentine "polymorphs": a discussion. *Amer. Mineral.* **55**, 1025-1047.

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